JP-A-9-95630

[Title of the Invention]

FIRE-RETARDANT COATING COMPOSITION, AND ELECTRIC WIRE OR ELECTRIC POWER CABLE COATED WITH THE SAME

[Abstract]

[Object]

To provide a fire-retardant coating composition excellent in the efficiency of preventing fire from spreading without emitting harmful gases in the case of a firing incident and suitable for forming a coating with good flexibility and water-proofness.

[Solving Means]

The fire-retardant coating composition contains a synthetic resin emulsion 20 to 40% by weight (on the basis of dry weight), a metal hydrate 30 to 70% by weight, clay and/or Sanpi (sepiolite) 1 to 9% by weight, and mica 5 to 20% by weight.

[Claims]

[Claim 1]

A fire-retardant coating composition containing a synthetic resin emulsion 20 to 40% by weight (on the basis of dry weight), a metal hydrate 30 to 70% by weight, clay and/or Sanpi (sepiolite) 1 to 9% by weight, and mica 5 to 20% by weight.

[Claim 2]

The fire-retardant coating composition according to claim 1, wherein the ratio of the synthetic resin emulsion contains an ethylene-vinyl acetate emulsion and an acrylic acid ester emulsion.

[Claim 3]

The fire-retardant coating composition according to claim 2, wherein the ratio of the acrylic acid ester emulsion is 1 to 50% by weight in the entire synthetic resin emulsion on the basis of dry weight.

[Claim 4]

The fire-retardant coating composition according to claim 1, wherein the metal hydrate is aluminum hydroxide and/or magnesium hydroxide.

[Claim 5]

An electric wire or an electric power cable having a coating of the fire-retardant coating composition according to claim 1 on the outer surface.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The invention relates to a non-halogen type fire-retardant coating composition, more particularly a fire-retardant coating composition excellent in efficiency of preventing fire from spreading, generating no harmful gas such as hydrochloric acid or the like even in a case of a firing incident, easy to apply, formable to give a coating excellent in flexibility and water-proofness, and usable as a coating material for preventing firing of electric wires and electric power cables.

[0002]

[Prior Art]

For an insulator and a sheath of an electric power cable, materials, for example, polyethylene and poly(vinyl chloride) have been used. However, since these materials are all flammable, they are fired in the case of a firing incident. At the time of firing, the fire is sometimes spread along the above-mentioned cable coatings to another room neighboring the site where the fire takes place to result in great expansion of the damages.

[0003]

Accordingly, countermeasures for preventing such an incident have been made for the cables. One method is forming

a coating of a composition foaming at the time of heating on the outer circumference of the cables so as to prevent fire from spreading through the coating. Another method is forming a coating of a non-foaming fire-retardant coating material on the outer circumference of the cables.

[0004]

As the fire-retardant coating material to be used for the latter method, there are a composition proposed in Japanese Patent Application Publication No. 57-35736 and a composition proposed in Japanese Patent Application Publication No. 58-28310. The former composition indispensably contains a synthetic resin emulsion such as ethylene-vinyl acetate emulsion, a non-fusible organic fiber, an inorganic powder containing clay and/or zinc borate, and a halo hydrocarbon.

[0005]

In the case of the coating of the composition, a considerably efficient flame retarding property is assured by the halogenated hydrocarbon and in the case of a firing incident, the clay and/or zinc borate contained in the composition forms a hard outer sheath by the heat to prevent the cable coating underneath from firing, resulting in fire prevention of fire from spreading. However, in the case of the coating, the halogenated hydrocarbon is costly and sometimes generates harmful gases such as hydrochloric acid

owing to the thermal decomposition. Further, in the case of mixing organic fibers, if relatively long fibers are mixed, for example, a spray gun is sometimes clogged at the time of spray coating. Further, when long fibers are mixed, pin holes are easily formed in the coating formed on the cable coating and moisture penetrates the cable coating through the pin holes to result in an adverse problem that the adhesion strength between the cable coating and the coating formed thereon is deteriorated.

[0006]

On the other hand, the latter composition indispensably contains an emulsion of ethylene-vinyl acetate copolymer, an inorganic fiber like asbestos, an inorganic powder of aluminum hydroxide, a halogenated hydrocarbon, and antimony trioxide. In the case of a coating of the composition, the coating is more excellent in the water-proofness and weathering resistance than the coating of the former composition and generates less harmful gases, however these properties are said to be insufficient.

[0007]

Further, in order to suppress harmful gas generation amount and maintain the effect to prevent fire from spreading through the cable, the mixing amounts of inorganic powders including a metal hydrate such as aluminum hydroxide may be increased, however with such a composition, the coating

formed from the composition loses flexibility, becomes brittle, and has no water-proofness and weathering resistance.

[0008]

[Problems to be Solved by the Invention]

The invention aims to solve the above-mentioned problems in conventional compositions for preventing fire expansion and provide a fire-retardant coating composition which is non-halogen type generating no harmful gases at the time of a firing incident and nevertheless which is efficient as a halogen type one to prevent fire from spreading, gives a coating excellent in flexibility, water-proofness and weathering resistance, and has good coatability and economical properties and electric wires and electric power cables coated with the fire-retardant coating composition.

[0009]

[Means for Solving the Problems]

In order to accomplish the above-mentioned aim, the invention provides a fire-retardant coating composition containing a synthetic resin emulsion 20 to 40% by weight (on the basis of dry weight), a metal hydrate 30 to 70% by weight, clay and/or Sanpi (sepiolite) 1 to 9% by weight, and mica 5 to 20% by weight and also the invention provides an electric wire or an electric power cable having a coating of the above-mentioned fire-retardant coating composition.

[0010]

[Embodiments of the Invention]

At first, the first inevitable component in the composition of the invention is a synthetic resin emulsion. The emulsion contains fine particles of synthetic resin dispersed in water in emulsion state and when dried, that is when water is removed, fine particles of the synthetic resin are melt-bonded one another to form a coating.

[0011]

The addition amount of the synthetic resin emulsion in the fire-retardant coating composition of the invention, on the basis of dry weight, that is when water is removed as described above, is set to be 20 to 40% by weight. If the mixing content is less than 20% by weight, the coating to be formed loses the flexibility and becomes brittle to result in a problem in water-proofness. On the other hand, if the addition amount exceeds 40% by weight, the resin component is so much to deteriorate the flame retarding property and makes the effect of preventing fire from spreading insufficient. It is preferably in a range of 25 to 35% by weight.

[0012]

As the synthetic resin emulsion to be used for the invention, conventionally known emulsions may be used and examples are water-based emulsions of vinyl acetate,

water-based emulsions of ethylene vinyl acetate copolymers (EVA), water-based emulsions of acrylic acid esters, water-based emulsions of vinyl acetate-vinyl chloride copolymers, water-based emulsions of ethylene-vinyl acetate-vinyl chloride ternary copolymers, water-based emulsions of synthetic rubber, and water-based emulsions of natural rubber. They may be used alone or mixtures of two or more of emulsions selected from them may be used.

[0013]

In the case of forming a coating of the composition of the invention on a coating of an electric wire or an electric power cable, those which can provide a coating excellent in water-proofness and weathering resistance are preferably used as the emulsion. Among the above-exemplified synthetic resin emulsion, in terms of the foregoing coatability, water-based emulsions containing EVA and acrylic acid ester coexisting therein are preferable.

[0014]

In such a case, the ratio of the dry weight of the emulsion of acrylic acid ester is preferably 1 to 50% by weight (accordingly the ratio of the dry weigh of the emulsion of EVA is 50 to 99% % by weight) in the entire dry weight of the emulsion. If the ratio of the acrylic acid ester emulsion is less than 1% by weight, the formed coating has no flexibility and becomes brittle and at the same time its

water-proofness and weathering resistance becomes insufficient to make it difficult to use the composition as the fire-retardant coating composition for cables. Further, when it becomes a high temperature, the strength of the coating is deteriorated and consequently it tends to easily occur that the coating is dropped at the time of a firing incident and the coating of the electric wire and electric power cable is exposed.

[0015]

In the case the ratio exceeds 50% by weight, the water-proofness and the weathering resistance of the coating are excellent, however the material costs high to result in disadvantage in terms of the economical property. It is preferably in a range of 10 to 20% by weight. Use of the emulsion with the ratio in the defined range enables the formed coating to maintain the shape as the coating even if the following second, third, and fourth indispensable components are added in respectively desired contents.

[0016]

A metal hydroxide as the second indispensable component in the composition of the invention releases crystal water contained in itself by thermal decomposition at the time of firing the coating and suppresses temperature increase of the coating (resin) existing underneath of the coating of the composition by the endothermic reaction at

that time and consequently shut the ignition or continuous combustion of the resin coating. Further, it generates steam at the time of dehydration reaction to dilute the combustion gas of the cable resin coating to inhibit further combustion.

[0017]

As such a metal hydrate, those which can release crystal water contained in themselves when being heated may be used and preferable examples are aluminum hydroxide and magnesium hydroxide. Particularly, aluminum hydroxide is preferable in terms of the cost. Such metal hydrates may be used alone or in the form of mixtures of two or more of them.

[0018]

In the case of mixing, it is effective to previously treat the metal hydrates with a silane coupling agent or the like for surface treatment since they can be dispersed evenly, however the surface treatment is not indispensable. The mixing amount of the metal hydrates in the entire composition (on the basis of the dry weight) is set to be 30 to 70% by weight on the basis of the weight in the case the water of the above-mentioned synthetic resin emulsion is removed.

[0019]

If the mixing amount is less than 30% by weight, the above-mentioned effect is not sufficiently exhibited to

result in deterioration of the flame retarding property of the coating and insufficient effect on prevention of fire from spreading. On the other hand, if it exceeds 70% by weight, the coating becomes inferior in the flexibility and brittle and it is sometimes peeled off the coating resin of the electric power cable. The mixing amount is preferably 40 to 60% by weight.

[0020]

The metal hydrate is added in form of a powder and in such a case, in consideration of uniform dispersion in a produced fire-retardant coating composition and assurance of a high flame retarding property of a coating to be formed, the powder is preferable to have an average particle diameter of 3 to 30 μm. As such a metal hydroxide, for example, CL-310 (trade name; aluminum hydroxide manufactured by Sumitomo Chemical Co., Ltd.), Kisuma 5A (trade name; manufactured by Kyowa Chemical Industry Co., Ltd.) can be exemplified.

[0021]

The third indispensable component in the composition of the invention is clay and/or Sanpi and the fourth indispensable component is mica. Only in the case the third indispensable component and the fourth indispensable component coexist in the composition, both can contribute formation of a hard outer sheath at the time of firing the coating and consequently prevent the flow of the resin owing

to fusion of the coating resin of the electric wire or electric power cable underneath the coating and prevent the fire from spreading.

[0022]

Such an effect cannot be actualized if only either one of the third indispensable component (clay and/or Sanpi) and the fourth indispensable component (mica) is contained and in the case the composition contains both, the effect is at first exhibited. The reason for that is not necessarily clear, however in general, it is supposed that since the clay is a hydrated silicate having a layer structure and Sanpi is a mineral with a composition described later and further mica is an aluminosilicate with a flat structure having cleavage planes, when they are heated, a kind of sintering reaction takes place among them to form a hard sheath.

[0023]

The clay between the third indispensable components may include those utilized conventionally for a variety of coating materials (e.g. kaolinite, talc, zeolites, Kanuma soil, and the like) and is not particularly limited. Further, as the clay, those produced by a dry, wet or firing method may all be used. The clay is added in form of granules, in such a case, if the granules are finer, they are dispersed more evenly in the composition and accordingly, at the time

of a firing incident on the formed coating, the above-mentioned outer sheath is evenly formed in the entire coating to improve the effect of preventing the fire from spreading. It is generally preferable to use granules with 2 μm or smaller.

[0024]

As such clay, for example, Burgess No. 10 (trade name; manufactured by Shiraishi Calcium Kaisha Ltd.) can be exemplified. Further, between the third indispensable components, Sanpi is one kind of clay minerals having a large number of hydroxyl groups in the surface and includes sepiolite, which is hydrated magnesium silicate, and attapulgite, which is hydrated magnesium aluminum silicate and is commonly called as mountain cork, mountain leather, or mountain wood. That is, in general, mass of magnesium silicate having the fibrous property and the mineral called as Kaihoseki by Japanese is also included.

[0025]

Sanpi shows the dry cohesion property itself and also cohesion of other dispersed powders when it is once dispersed in water and then the obtained dispersion is dried. Sanpi is sintered to be a ceramic and thus hardened and keeps the shape when the cohering body is fired.

[0026]

Accordingly, if the above-mentioned Sanpi is added

to the composition of the invention, the formed coating keeps the shape owing to the dry cohesive of Sanpi and at the time of a firing incident, Sanpi becomes a ceramic to form a hard outer sheath to efficiently prevent firing of the coating resin of the electric wire or the electric power cable underneath the coating from spreading. Further, the shape of Sanpi is not particularly limited and may have a fibrous, a plate-like or a granular shape.

[0027]

In the case of using fibrous Sanpi, one having a fiber length of 10 cm or shorter and a fiber diameter of 0.5 to 50 μm is preferable to be used and one having a fiber length of 0.1 to 5 cm or shorter and a fiber diameter of 5 to 10 μm is more preferable to be used. In the case of such fibrous Sanpi, it may be bundled or about 10 to 200 fibers are bundled into one.

[0028]

In the case of using plate-like or granular type Sanpi, one having a granular size of 5 to 350 meshes (Tyler sieve) is preferable. As such Sanpi, for example, Aid Plus (trade name; Mizusawa Industrial Chemicals Ltd.) can be exemplified. With respect to the third indispensable component, the clay and Sanpi may be used each alone and in the form of a mixture of each other. However, as described above, owing to the peculiar function of Sanpi, a desirable outer sheath can

be formed at the time of a firing incident and a large quantity of the metal hydrate can be added and accordingly, a coating excellent in prevention of fire from spreading can be formed and therefore, Sanpi is preferable to be added as the third indispensable component.

[0029]

In the case of adding clay and Sanpi as third indispensable components, the mixing ratio of both is not particularly limited and in terms of easy coating formability and less probability of the outer sheath from dropping at the time of a firing incident, it is preferably to mix clay 4 to 9% by weight and Sanpi 2 to 9% by weight. Mica, the fourth indispensable component, is a substance in which a large number of flat crystal pieces are laminated, for example, in the case water is goring to penetrate the inside from the coating, the water penetration path is long and therefore, water hardly reaches the inside and as a result, mica contributes to improvement of the water-proofness of the coating.

[0030]

If mica is pulverized, the shielding effect against the water penetration from the outside of the coating is weakened and the viscosity of the composition is sharply increased to make spray coating difficult. Further, since mica has a flaky crystal structure, it is difficult to

pulverize the mica into finely powder in terms of production. Accordingly, mica having an average particle diameter of 40 to 150 μm is used.

[0031]

As the mica to be used for the invention, for example, B-92 (trade name; manufactured by Yamaguchi Mica Ind. Co., Ltd.) can be exemplified. The mixing ratios of the third indispensable component and the fourth indispensable component are set to be 1 to 9% by weight and 5 to 20% by weight, respectively, and more preferably 4 to 9% by weight and 7 to 15% by weight, respectively.

[0032]

If the mixing ratios are less than the lower limit values of the above-mentioned ranges, the outer sheath formability becomes insufficient at the time of a firing incident occurring upon the formed coating and the effect of preventing the fire from spreading is deteriorated. Further, the produced coating is easy to drip to make it difficult to form a thick coating when the coating is applied to the coating resin of the electric wire or the electric power cable and as a result, the effect of the coating preventing the fire from spreading is deteriorated. Further since the addition amount of mica is so small as to deteriorate the water-proofness of the formed coating and gradually cause separation the coating resin of the

electric wire and the electric power cable and the formed coating.

[0033]

On the other hand, the mixing ratios of these components exceed the upper limits of the above-mentioned ranges, the viscosity of the produced fire-retardant coating composition becomes so high to make the spray coating and brush application difficult and make it difficult to form a coating with an even thickness. If in the case the viscosity is decreased by adding water further to the above-mentioned composition in order to increase the coatability, the composition is surely provided with good coatability, however a large amount of water has to be added and therefore, shrinkage of the coating to be formed rather considerably takes place and in an extreme case, cracks are formed in the coating and accordingly, the composition can not be a coating material.

[0034]

The fire-retardant coating composition of the invention can be produced by mixing the above-mentioned components in prescribed amounts, respectively, to be a coating material with a desired viscosity. At that time, based on the necessity, a proper amount of water may be added to adjust the viscosity. The obtained coating material is practically used for coating an object such as the electric

wire or the electric power cable by a common coating method, such as spray coating or brush application.

[0035]

[Examples]

Examples 1 to 11 and Comparative Examples 1 to 10

The components shown in Table 1 were mixed at the described ratios (% by weight) to obtain the respective coating materials. The respective components shown in Table 1 were as follows.

*1: trade name; Voncoat 2315 (solid matter 55% by weight, manufactured by Dainippon Ink and Chemicals, Inc.)

[0036]

*2: trade name; Voncoat EC-877 (solid matter 49% by weight, manufactured by Dainippon Ink and Chemicals, Inc.)

*3: trade name; Polysol S-500 (solid matter 50% by weight, manufactured by Showa Highpolymer Co., Ltd.)

*4 trade name; CL-310 (the average particle diameter 10 μm; manufactured by Sumitomo Chemical Co., Ltd.)

[0037]

*5 trade name; Kisuma 5A (the average particle diameter 0.8 μm; manufactured by Kyowa Chemical Industry Co., Ltd.)

*6 trade name; Zinc Borate 2335 (manufactured by US Borax Co.)

*7 trade name; Empara 70 (chlorine content 70% by weight, manufactured by Ajinomoto Co., Ltd.)

*8 trade name; AFR1001 (bromine content 87% by weight, manufactured by Asahi Glass Co., Ltd.)

*9 trade name; ATOX S (manufactured by Nippon Mine Refining Co., Ltd.)

[0038]

*10 trade name; Burgess No. 10 (the average particle diameter 0.5 μm; manufactured by Shiraishi Calcium Kaisha Ltd.))

*11 trade name; Aid Plus (Sepiolite manufactured by Mizusawa Industrial Chemicals Ltd.)

*12 trade name; B-92 (manufactured by Yamaguchi Mica Ind. Co., Ltd.)

*13 trade name; PK#50 (manufactured by Maruo Calcium Co., Ltd.)

[0039]

*14 trade name; Super S (the average particle diameter 4.2 μm; manufactured by Maruo Calcium Co., Ltd.)

*15 fiber with a thickness of 1 to 5 denier cut into 2 to 5 mm length.

The respectively produced coating materials were applied by brush application to electric power cables coated with an insulator and a sheath both made of polyethylene to form coatings each having a thickness of about 1 mm after drying. With respect to the coatings, the effect of preventing fire from spreading, the flexibility, the generation amount of the hydrochloric acid gas, and the

water-proofness were investigated by the following manners.

[0040]

The effect of preventing fire from spreading: a coating was heated by a propane gas burner for 10 minutes to form an outer sheath of the coating and the state of the outer sheath was observed. The sign o was marked in the case the state that the outer sheath of the coating was not dropped and covered the electric power cable and the sign X was marked in the case the state that the outer sheath was opened or dropped. The coating material which was marked with o in the above-mentioned test was newly applied to the above-mentioned coating resin of the electric power cable and then dried to form a coating with a thickness of about 1 mm after drying and the formed coating was subjected to the vertical tray combustion test standardized in IEEE 383 to mark the coating which gave an outer sheath scarcely dropping and showed good combustion properties with ◎.

[0041]

Flexibility: The state of the coating in the case of the electric power cable was bent was observed. In the case neither breaking nor cracking was formed in the coating, the sign o was marked, and in the case either breaking or cracking was formed in the coating, the sign X was marked.

Hydrochloric gas generation amount: Measurement was carried out according to a method standardized in JCS C No. 53 and

in the case the hydrochloric acid gas generation amount was 30 mg/g or less, the sign ○ was marked and in the case the amount exceeded 30 mg/g, the sign × was marked.

[0042]

Water-proofness: After the electric power cable was immersed in water at a normal temperature for 100 hours, the coating state and the adhesion strength of the coating to the electric power cable were observed. In the case no cracking was caused in the coating and the coating had good appearance, the sign ○ was marked and in the case cracking occurred and the coating had inferior appearance, the sign × was marked. Further, each coating material was investigated also for the coatability by spray coating using an air-less spraying apparatus. In the case spraying was carried out, the sign ○ was marked and in the case spraying was not carried out because of clogging of the nozzle, the sign × was marked. In the case the coating material was dripped after spraying, the dripping was marked.

[0043]

The results of the above-mentioned evaluations are shown collectively in Table 1 and Table 2.

[0044]

[Table 1] (omitted)

[0045]

[Table 2] (omitted)

[0046]

Table 1 and Table 2 make the following clear.

(1) At first, the compositions of the invention did not generate hydrochloric acid gas at the time of firing and thus were excellent in the safety, unlike compositions of Comparative Examples 1 to 3 and Comparative Example 10.

(2) The coatings made of the compositions were excellent in the effect of preventing fire from spreading and flexibility as same as or slightly higher than coatings made of the compositions containing conventionally known flame retarding agents (halogen type hydrocarbons) of Comparative Examples 1 to 3 and Comparative Example 10.

[0047]

(3) The coatings made of the compositions had more excellent water-proofness than the coatings made of the compositions of Comparative Examples 1 to 3 and Comparative Example 10 and thus former coatings could maintain the flame retarding property of electric power cables for a long duration.

(4) Further, coating materials containing the compositions of the invention were excellent in the coatability and the processibility for electric power cables.

(5) As it is made clear by comparison of respective Examples with Comparative Example 5 and Comparative Example 6, the above-mentioned properties of the compositions of the invention were at first derived from addition of clay and

mica in combination. Moreover, even in such a case, if the addition amount of aluminum hydroxide was increased, both of the effect of preventing fire from spreading and the flexibility were deteriorated as it is made clear from Comparative Example 7.

[0048]

(6) As it is made clear by comparison between Example 7 and Example 8 (sepiolite was added to the composition of Example 7), the coating of the composition containing Sanpi (sepiolite) was remarkably excellent in the effect of preventing fire from spreading.

(7) However, as it is made clear by comparison between Example 11 and Comparative Example 9, if the addition amount of sepiolite was so much, the effect of preventing fire from spreading and the flexibility were deteriorated.

[0049]

(Effects of the Invention)

As it is made clear from the above descriptions, a coating made of the fire-retardant coating composition according to claim 1 scarcely generates harmful gases such as hydrochloric acid gas, forms a hard outer sheath to prevent a resin underneath from melting and flowing out and accordingly the coating can prevent fire from spreading in the resin at the time of a firing incident.

[0050]

Further, the composition gives a coating with excellent flexibility and can be applied without dripping by spray coating or brushing application at the time of forming the coating and thus has excellent processibility. In the case of the fire-retardant coating compositions according to claims 2 and 3, the water-proofness and weathering resistance are made good and the formed coatings maintain such properties for a long duration.

[0051]

Further, since the electric wire or the cable according to claim 5 comprises the coating of the fire-retardant coating composition having the above-mentioned effect and formed on the surface, the damages following the fire expansion at the time of a firing incident can be suppressed.